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(54) Chemically modified lignin materials and their use in controlling fluid loss

(57) A polymeric composition for reducing fluid loss in drilling muds and cement compositions used in the recovery of oil and gas is obtained by free radical initiated polymerization, in an aqueous admixture, of

(a) lignin, modified lignins, lignite, brown coal, modified brown coal, or mixtures thereof, and,
(b) at least one water-soluble vinyl monomer chosen from the group consisting of (meth) acrylic acid, (meth) acrylamide, hydroxyethyl acrylate, hydroxypropyl acrylate, vinyl acetate, methyl vinyl ether, ethyl vinyl ether, N-methyl (meth) acrylamide, N,N-dimethyl (meth) acrylamide, vinyl sulfonate, and 2-acrylamido-N-methylpropane sulfonic acid, and then recovering said polymeric composition.

CHEMICALLY MODIFIED LIGNITE

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This invention relates to polymeric compositions for reducing fluid loss in drilling fluids and cement compositions used in oil and gas recovery and methods of controlling fluid loss from such drilling fluids and cement compositions.

Compositions useful in preventing fluid loss from wells being drilled using various kinds of drilling fluids such as fresh water muds, fresh water muds contaminated with calcium, or other multivalent cations, sea water muds, gypsum muds or lime muds have been taught in patents such as U.S. 4,678,591, Giddings, et al. Fluid loss from various kinds of cement applications in a drilled well have also been taught, for example in U.S. Patent 4,676,317, Fry et al, and in references cited within these two patents.

Compositions in these teachings are compositions in which lignins or modified lignins are alleged to have been polymerized using specific types of acrylic or vinyl monomers and modified in a way that would indicate that the lignin itself has been changed by grafting onto the lignin, lignite, or derivatized cellulose, various synthetic polymer branches pendant to the lignite structures. Lignin and lignite, for example in the U.S. 4,676,317 patent referenced above, was taught to be grafted by at least one member selected from the group of homopolymers, copolymers or terpolymers of 2-acrylamido-2-methylpropane sulfonic acid, acrylonitrile, N,N-dimethylacrylamide, acrylic acid, N,N-dialkylaminoethylmethacrylate and their water-soluble salts.

Reference to acids includes the metal salts thereof, particularly alkali metal or alkaline earth metal salts, as well as such other common salts such as ammonium salts, amine salts, quaternary amine salts, and the like. Reference to cationic amine monomers also is meant to include the acid salts or quaternary salts thereof.

These homopolymers, copolymers and terpolymers which are grafted onto the lignin/lignite according to the teachings of Fry, are anionic, cationic or both anionic and cationic. When anionic, they are anionic by incorporation of the sulfonic acid monomer or by incorporation of acrylic acid or its salts. When cationic, they are made cationic by the incorporation of the N,N-dialkylaminoethylmethacrylate monomer or its salts. Fry does not teach neutral species and requires the use of expensive monomer units. Fry also requires the use of acrylonitrile, a monomer which is primarily thought to be water-insoluble rather than water-soluble, although its solubility can be increased in water solutions containing other water-soluble vinylic monomers.

The present invention relates to compositions which are useful for both fluid loss additives and fluid loss controls when incorporated in oil field aqueous drilling muds or fluids at ambient and/or at elevated temperatures. The additives of this invention may serve in a wide range of drilling fluid types including fresh water muds, fresh water muds that are contaminated with multivalent ions such as calcium, sea water muds, gypsum muds, and lime muds, and the like. In addition, the compositions of the instant invention may also provide for fluid loss controls when used in formulations for aqueous cementing compositions when these cement formulations are used in oil and gas wells and the like.

Our compositions are those compositions which can be manufactured by the vinyl free radical polymerization of at least one water-soluble vinyl monomer chosen from the group consisting of (meth)acrylic acid, (meth)acrylamide, hydroxyethyl acrylate, hydroxypropyl acrylate, vinyl acetate, methyl vinyl ether, ethyl vinyl ether, N-methyl(meth)acrylamide, N,N-dimethyl(meth)acrylamide, vinyl sulfonate, and 2-acrylamido-2-methylpropane sulfonic acid. This

polymerization achieves water-soluble polymers, such as homopolymers, copolymers, terpolymers, and potentially achieves polymer modification, such as graft polymers, of the lignins or lignites used in combination or in the presence of the monomeric reactants listed above which are being free radically polymerized.

Lignin, modified lignins, lignite, brown coal, or modified brown coals must always be present during the polymerization of the above monomers by free radical catalysts using typical catalysts for this purpose. These lignins, modified lignins, lignites, brown coal, and the like fall within a generic description of chemical structures, the original structure of which is derived from vegetable products such as wood products either by degradation, extraction or long-term biological degradation as in formation of brown coal, humate deposits, and the like. These lignin materials are preferably causticized, or otherwise peptized, prior to use, such causticization providing for the formation of aqueous solutions and/or aqueous colloidal suspensions of the lignin or lignite materials. Other related lignin type materials are leonardite which is a naturally oxidized product with higher oxygen and moisture content than lignite, as well as humic acid, a complex polycyclic polycarboxylic acid which can also be converted into its basic salt forms by reaction with base salts of alkali metals, alkaline earth metals, ammonia or amines. These types of lignin/lignite/humate or other like materials may also be modified, such as by being sulfonated. Such products, as well as derivatives of these lignin or humate acid products, are described in U.S. Patent No. 3,266,887.

The polymerization in the presence of these lignin or lignite materials either causticized or modified in other ways or both, is prepared in accordance with the teachings of U.S. Patent No. 4,502,964. The reaction temperatures and times may be varied, with the reaction

time being temperature dependent, for example, the higher the temperature, the shorter the reaction time. Generally, temperatures are employed within the range of about 35°C to about 90°C with reaction times varying as necessary according to the amounts of catalysts used, ratio of reactants, methods of addition of monomers, and the like. Routine experimentation may be used to optimize the process that obtains compositions of this invention.

As indicated, these compositions are prepared by conducting the polymerization in the presence of the lignins, causticized lignin, or causticized lignite, modified lignin, brown coal, or modified brown coal. The amount of brown coal, lignin type materials, and such, that can be combined with the monomer or monomer mixture used in the polymerization process can range between about 5% to about 90% by weight, preferably between about 20% and 50% by weight, and most preferably between about 20-40% by weight.

The use of the polymers obtained by the reaction of the monomers described above in the presence of the lignin or modified lignin, or lignites and the like, provide excellent results at dosages ranging between about 0.1 to about 10 lbs. per barrel, with preferred dosages ranging between about 1-5 lbs. per barrel of drilling fluid.

Dosages are varied depending upon the conditions and type of formation being treated as well as the type of mud being used, as described above, or the type of cement being used under varying conditions.

The water-soluble vinyl monomers that are useful in the practice of this invention are those monomers which are useful to obtain the modified lignin/lignite compounds by completing, using free radical initiation techniques, a vinylic polymerization in the presence of the lignins described above. Preferably, the lignins have been causticized or otherwise peptized so that the solution or

suspension of modified or causticized lignins or lignites appears as a dark solution or colloidal suspension of these materials. To these suspensions/solutions are added at least one of the water soluble vinyl monomers mentioned above which are useful for the practice of the invention described above. These monomers are such water-soluble vinyl monomers as acrylic acid, methacrylic acid, acrylamide, methacrylamide, hydroxyethyl acrylate, hydroxypropyl acrylate, vinyl acetate, methyl vinyl ether, ethyl vinyl ether, N-methyl acrylamide, N-methyl methacrylamide, N,N-dimethyl acrylamide, N,N-dimethyl methacrylamide, vinyl sulfonate, 2-acrylamido-2-methylpropane sulfonic acid, and the like. These monomers are used primarily wherein the weight ratio of the lignin or modified lignin or lignites used in the polymerization relative to the amount of water-soluble vinylic monomers used ranges between about 8:2 to about 2:8.

The amount of water-soluble vinyl monomer described above can include the use of a single monomer, two monomers, three separate monomers, or more. Such use permits the synthesis of modified lignins or admixtures of lignins with polymers which derive from the formation of a homopolymer, a copolymer, a terpolymer, or a more complex combination polymer containing four or more monomers as described. Such reaction product may also include graft polymers of the lignin or modified lignin base reactant, such graft polymers derived from the use of the monomer or admixture of monomers listed above.

The monomers must be water-soluble or, in the case of, for example, vinyl acetate, a methyl vinyl ether and ethyl vinyl ether, the initial water solubility, though somewhat low, can be improved by combining these materials in the presence of aqueous solutions of other of the vinylic monomers listed.

The weight ratio of the lignins, modified

lignins, causticized lignite, brown coal, modified brown coal, or mixtures thereof, are normally present in the admixture with the chosen monomers at a ratio ranging from about 8:2 to about 2:8, such weight ratio achievable either upon initiation of polymerization or achievable by the incremental or continuous addition of prescribed monomers in a way so that at the end of the addition of the monomer to the admixture, these ratios have been achieved.

The preferred admixture contains a causticized lignite in combination with an admixture of from 5-100 mole percent of (meth)acrylic acid and from about 95-0 mole percent of (meth)acrylamide. When using the term (meth) acrylic acid to describe the monomer used, I intend this to mean that I have used or can use acrylic acid, methacrylic acid, or any admixture of acrylic acid and methacrylic acid from 100-0 to 0-100 weight percent. Similarly, when using the term (meth)acrylamide, I mean to indicate that I may use acrylamide, methacrylamide, or any admixture of acrylamide and methacrylamide within the same ranges as above mentioned.

We have found that the preferred species mentioned above, that being a reaction product derived from reacting causticized lignite with admixtures of (meth)acrylic acid and (meth)acrylamide provide a product having greater activity, at a lower cost, than the admixtures taught in the prior art. In addition, the monomer materials are more readily available from a commercial standpoint and do not require complicated polymerizations in regard to the combination of essentially water-soluble and essentially water-insoluble species.

Polymerization is accomplished by free radical initiation using standard peroxide or hydroperoxide catalysts or alternatively, redox systems such as bisulfite and persulfate systems, or such other free

radical initiators known in the art. One could most likely initiate this polymerization by using any technique that generates free radicals, perhaps UV light, perhaps radiation, or other free radical generating techniques known to the artisan.

A most preferred composition useful as a fluid loss additive as described above is that composition prepared by reacting, in an aqueous admixture, from 15-30 weight percent causticized lignite with from 85-70 weight percent of a vinylic monomer mixture having from 20-80 mole percent acrylic acid and from 80-20 mole percent acrylamide, said aqueous admixture containing, on a total solids basis, from 5-95 weight percent of the sum of the causticized lignite and the vinylic monomer mixture. After polymerization is completed, either using a batch technique, or using a technique that requires the incremental or continuous addition of monomers to a vessel containing the peptized or causticized lignite in aqueous suspensions/solutions, preferably having contained therein appropriate radical catalyst systems, the polymer solution or suspension in water or aqueous solvents is then dried to obtain a dried composition containing the appropriate amounts of lignins or lignites and the vinyl monomer ratios of polymers either adducted to the lignin or lignite backbone or admixed with the lignin or lignite backbone, or admixtures thereof, as the case may be.

The formation of these compositions permits an improved method for controlling the fluid loss and rheology stabilization of clay-containing aqueous oil well drilling muds and of improving fluid loss from well cementing compositions which method comprises adding to said drilling muds or to said cementing compositions, an effective fluid loss controlling amount of a polymeric composition obtained by free radical initiated polymerization, in aqueous admixture, of the ingredients:

- (a) At least one of a lignin, modified lignin,

lignite, causticized lignite, brown coal, and modified brown coal, in admixture with

(b) At least one water soluble vinyl monomer chosen from the group consisting of (meth)acrylic acid, (meth)acrylamide, hydroxyethyl acrylate, hydroxypropyl acrylate, vinyl acetate, methyl vinyl ether, ethyl vinyl ether, N-methyl(meth)acrylamide, N,N-dimethyl(meth)acrylamide, vinyl sulfonate, and 2-acrylamido-2-methylpropane sulfonic acid, and the like.

Preferably, a method of improving fluid loss and rheology stabilization of clay-containing aqueous oil drilling muds and of improving fluid loss from well cementing compositions include the use of the lignin, modified lignin, causticized lignite, and the like, in aqueous admixture with at least one of the above listed vinyl monomers wherein the weight ratio of the lignin component to the water-soluble vinylic monomer component ranges between about 8:2 to about 2:8, preferably to about 7:3 to about 2:8, and most preferably, wherein the ratios of the lignin, modified lignin, causticized lignite and the like component ranges between about 2:8 to about 7:3 relative to an admixture of water-soluble vinyl monomers containing from 5-100 mole percent (meth)acrylic acid and from about 95-0 mole percent of (meth)acrylamide. In a particularly preferable method of practicing the invention, the vinylic monomer admixture contains from about 20-80 mole percent acrylic acid, and from about 80-20 mole percent acrylamide and wherein an aqueous admixture having from 10-70 weight percent total solids, prior to initiation by vinylic free radical catalysts, contains on a solids basis, from 15-30 weight percent of causticized lignite, and from about 85-70 weight percent of the mixture of acrylic acid and acrylamide.

The polymeric composition found to be most useful in the practice of the method of controlling fluid loss in various clay-based drilling muds, as described above, is

obtained from a composition wherein from 20-30 weight percent causticized lignite is reacted with from about 80-70 weight percent of a mixture of from 50-80 mole percent acrylic acid and from about 50-20 mole percent acrylamide wherein the aqueous admixtures contains from 20-60 weight percent of the sum of the causticized lignite and mixture of acrylic acid and acrylamide monomer units.

Another preferred mixture, which has found use particularly in sea water drilling muds, is a polymeric composition obtained from free radical initiation of an aqueous mixture containing from 10-70 weight percent of the sum of

- (a) from 15-35 weight percent causticized lignite, and
- (b) from 85-65 weight percent (meth)acrylic acid.

Again, the term (meth)acrylic acid means acrylic acid, or methacrylic acid, or any admixtures of acrylic acid and methacrylic acid.

EXAMPLES

Example 1 As an example of the formulation of the polymers of this invention, the following formulation and procedure is given. The following raw materials were charged to a reaction vessel equipped with a heating source, a nitrogen blanket capability, a condenser, a mixer/stirrer, a thermometer, or other means of measuring temperature, and means for transferring reactants into the vessel. 52.39 weight percent of deionized water was charged to the vessel followed by the slow addition of 3.98 weight percent of a causticized lignite. These materials were mixed at approximately 45°C for approximately one hour. To this admixture was added an aqueous solution of acrylic acid which had been neutralized with a 50% sodium hydroxide solution such that the admixture now contained an additional 9.49 weight percent deionized water, 3.18 weight percent acrylic acid and 3.41 weight percent of the 50% sodium hydroxide. To

this admixture was also added 26.48 weight percent of a 48.2% solution in water of an acrylamide monomer. These materials then had added to them EDTA, sodium bisulfite, and ammonium persulfate such that these ingredients comprised 0.07 weight percent EDTA in the vessel, 0.50 weight percent sodium bisulfite and 0.50 weight percent ammonium persulfate for a total in the vessel of 100 weight percent. The pH was adjusted to a pH ranging anywhere from between about 7.0 to about 10.0. The reaction contents were cooled to room temperature and one-third of the combination sodium bisulfite, ammonium persulfite mixture was added. An exotherm, indicating polymerization occurred, which, after it naturally cooled, the rest of the catalyst was added incrementally over a period of about one to four hours. After all of the catalyst was added to the vessel, while stirring, over a nitrogen purge, additional reaction time at the temperature last achieved by the last exotherm following the addition of catalyst was permitted. This additional reaction time can be as short as 15 minutes and may be as long as two hours or more.

The polymers formed by the above type of procedure can be used in the solution in which the polymerization has been run or may be dried and used in powder or pellet form.

The following tests indicates the types of materials that were synthesized and tested. Polymer 1 contained 20 weight percent causticized lignite and 80 weight percent of an acrylamide/acrylic acid (as the sodium salt) admixture which contained 80 mole percent acrylamide and 20 mole acrylic acid salts. Polymer 2 again contained 20 weight percent lignite and 80 weight percent of an admixture of acrylamide and acrylate salt having a mole ratio of 70-30. Polymer 3 contained 20 weight percent lignite and 80 weight percent of a ratio of acrylamide/acrylate of 60/40. Polymer 4 contained 20

weight percent lignite and 80 weight percent of a mixture having the mole ratio of 50/50 acrylamide/acrylate salt. Polymer 5 contained 20 weight percent lignite and 80 weight percent of a 20/80 mole ratio of an acrylamide/acrylate. Polymer 6 contained 20 weight percent lignite and 100 weight percent sodium acrylate. Polymer 7 contained 30 weight percent lignite and 70 weight percent of an 80/20 mole ratio mixture of acrylamide and sodium acrylate. Polymer 8 contained 20 weight percent modified lignite and 80 weight percent of a 80/20 mole ratio mixture of acrylamide and sodium acrylate. Polymer 8 was manufactured with a sulfomethylated lignite compound.

EXAMPLE 2

Using Polymers 1-8 as described above, the plastic viscosity yield point, gel strength, and fluid loss measured over a 30 minute time period were compared according to test procedures described in the API publication PR-13-B.

Two types of drilling muds were formulated. Mud 1 contained 340 lbs. per barrel tap water, 20 lbs. per barrel bentonite clay, 50 lbs. per barrel rev dust, and 10.6 lbs. per barrel sea salt. This mixture was admixed until consistent. Mud 1 had a pH of 9.0, as modified with common pH adjusting chemicals.

Mud 2 contained 245 lbs. per barrel tap water, 10 lbs. per barrel bentonite clay, 50 lbs. per barrel rev dust, 6 lbs. per barrel chrome lignosulfonate, 400 lbs. per barrel barite, 10.5 lbs. per barrel sea salt, which formulation was admixed to consistency and pH adjusted to a pH of 10.0.

Rev dust is a simulated drilled solid which is a ground, low-yielding, non-swelling clay made available for these test purposes.

Both Mud 1 and Mud 2 formulations were aged at 250°F overnight and the following fluid loss tests were

run.

The results given in Table 1 use Mud 1 with fluid loss measured by a standard API fluid loss test described in the API publication RP-13-B. This test is run at room temperature at 100 psi. The polymers tested reduced the fluid loss as well as the yield point and gel strengths of the mud, although some polymers were more effective as dispersants for the mud.

Table I

Sample	Active Conc. (PPB)	PV	YP	10 Sec/10 Min GELS	API (ml)
Blank		6	16	17/35	50
Resinex	4	6	11	12/20	44
Resinex	6	6	7	6/18	30
Resinex	8	7	3	2/14	17
Polymer A	2	7	4	3/21	30
Polymer A	3	9	3	2/16	22
Polymer 1	2	7	3	3/16	43
Polymer 1	3	6	1	1/2	40
Polymer 4	1	7	9	9/19	40
Polymer 4	2	7	6	3/15	25
Polymer 4	3	8	1	0/2	16.5
Polymer 5	1	7	10	11/19	42
Polymer 5	2	7	11	10/21	31
Polymer 5	3	7	8	6/21	20
Polymer 6	1	8	13	12/14	47
Polymer 6	2	6	11	8/13	38

A high-temperature, high-pressure test was also given to the polymers described above. This test is run at a temperature of about 350°F, 500 psi, and the fluid loss numbers are corrected according to standard procedures. The results in Table II use Mud 2 which contains barite, a barium sulfate weighting agent typically used in these kinds of base muds when higher temperatures and higher pressures are encountered in the

drilling operation.

Table II

<u>Sample</u>	<u>Active Conc. (PPB)</u>	<u>PV</u>	<u>YP</u>	<u>10 Sec/ /10 Min GELS</u>	<u>API (ml)</u>	<u>HTHP (ml)</u>
Blank*		35	10	4/43	22	dry
Resinex*	2	32	15	4/38	7	dry
Resinex*	4	37	17	3/40	5	54
Resinex*	6	38	16	3/40	4	36
Resinex*	8	37	21	5/43	3	16
Polymer A*	2	47	23	4/37	8	50
Polymer 1	1	37	12	3/26	11	74
Polymer 1	2	46	5	2/3	5	30
Polymer 1	3	54	11	2/4	4.5	20
Polymer 2	2	58	14	2/7	8	42
Polymer 2	3	63	25	3/9	6.5	23
Polymer 3	2	54	19	2/14	8	42
Polymer 3	3	65	26	2/18	6	24
Polymer 4	2	52	22	3/19	11	54
Polymer 5	2	48	3	2/24	12	75
Polymer 7	2	46	1	1/2	5	44
Polymer 7	3	50	8	2/3	4.5	26
Polymer 8	2	45	2	1/2	5.5	42
Polymer 8	3	50	9	2/5	4	23

*2 pounds per barrel of additional chrome lignosulfonate were added to these muds, after aging to lower gel strengths.

Table II presents both high-temperature, high-pressure fluid loss as well as fluid loss at ambient temperatures according to the API test above described.

In the Tables above, Resinex represents a commercial sample available from MI Industries which sample is believed to be a condensed reacted product derived from the condensation of a sulfonated lignite condensed with a resin derived from phenol-sulfonic acid, formaldehyde reaction. Polymer A is exactly the polymer

described in U.S. 4,678,591.

If one were to use the compositions described above in cementing compositions to derive improved fluid loss capabilities for use in ambient or elevated temperature environments in oil, gas and water well cementing operations, one would expect to observe improved fluid loss results for cementing operations as is described above for drilling fluids and drilling muds. Also, one would expect to derive improved results, relative to commercial samples currently available, when using these polymers in any of the fresh water muds, contaminated with multivalent cations such as calcium and the like, sea water muds as described above, gypsum muds and/or in lime muds.

CLAIMS

1. A polymeric composition for reducing fluid loss in drilling muds and cement compositions used in the recovery of oil and gas which is obtained by free radical initiated polymerization, in an aqueous admixture, of

(a) lignin, modified lignins, lignite, brown coal, modified brown coal, or mixtures thereof, and

(b) at least one water-soluble vinyl monomer chosen from the group consisting of (meth)acrylic acid, (meth)acrylamide, hydroxyethyl acrylate, hydroxypropyl acrylate, vinyl acetate, methyl vinyl ether, ethyl vinyl ether, N-methyl(meth)acrylamide, N,N-dimethyl(meth)acrylamide, vinyl sulfonate, and 2-acrylamido-2-methylpropane sulfonic acid, and wherein the weight ratio of a:b is within the range of from about 8:2 to about 2:8, and then recovering said polymeric composition.

2. The polymeric composition of claim 1, wherein the weight ratio of a:b is between about 7:3 to about 2:8; and the (a) is causticized lignite and the (b) is an admixture of from 5-100 mole percent of (meth)acrylic acid and from 95-0 mole percent of (meth)acrylamide.

3. The polymeric composition of claim 2, wherein the polymeric composition is obtained by free radical polymerization of an aqueous admixture of

(a) 15-30 weight percent causticized lignite, and

(b) 85-70 weight percent of a vinylic monomer mixture having from 20-80 mole percent acrylic acid and from 80-20 mole percent acrylamide, said aqueous admixture containing from 5-95 weight percent of the sum of (a+b).

4. The polymeric composition obtained by drying the compositions of claims 1, 2 or 3.

5. A method of improving fluid loss and rheology stabilization of clay containing aqueous oil drilling muds and of improving fluid loss from well cementing compositions which comprises adding to said drilling muds

or cementing compositions an effective fluid loss controlling amount of a polymeric composition obtained by free radical initiated polymerization, in aqueous admixture, of the ingredients:

(a) at least one of lignin, modified lignin, lignite, causticized lignite, brown coal, and modified brown coal, and,

(b) at least one water-soluble vinyl monomer chosen from the group consisting of (meth)acrylic acid, (meth)acrylamide, hydroxyethyl acrylate, hydroxypropyl acrylate, vinyl acetate, methyl vinyl ether, ethyl vinyl ether, N-methyl(meth)acrylamide, N,N-dimethyl(meth)acrylamide, vinyl sulfonate, and 2-acrylamido-2-methylpropane sulfonic acid, and wherein the weight ratio of a:b is within the range of from about 8:2 to about 2:8, and then recovering said polymeric composition.

6. The method of claim 1, wherein the polymeric composition is obtained from an aqueous admixture containing from about 2:8 to about 7:3 of (a):(b), and b is an admixture of from 5-100 mole percent (meth)acrylic acid and from about 95-0 mole percent of (meth)acrylamide.

7. The method of claim 5, wherein the polymeric composition is obtained from an aqueous admixture containing from 5-95 weight percent of the sum of

(a) 15-30 weight percent causticized lignite, and
(b) 85-70 weight percent of a mixture having from 20-80 mole percent acrylic acid and from 80-20 mole percent acrylamide.

8. The method of claim 7, wherein the polymeric composition is obtained from an aqueous admixture containing from 10-70 weight percent of the sum of

(a) from 20-30 weight percent causticized lignite, and
(b) from 80-70 weight percent of a mixture having from 50-80 mole percent acrylic acid and from 50-20

mole percent acrylamide.

9. The method of claim 5, wherein the polymeric composition is obtained from an aqueous admixture containing from 10-70 weight percent of the sum of

(a) from 15-35 weight percent causticized lignite, and

(b) from 85-65 weight percent (meth)acrylic acid.

10. The polymeric composition for reducing fluid loss in drilling muds and cement compositions used in the recovery of oil and gas which is obtained by free radical initiated polymerization substantially as herein described with reference to the accompanying examples.

11. The method of improving fluid loss and rheology stabilization of clay containing aqueous oil drilling muds and of improving fluid loss from well cementing compositions substantially as herein described.

12. Compositions including drilling muds when produced by a method as claimed in any one of claims 5 to 9 and 11.